Prediction of large bias-dependent magnetoresistance in all-oxide magnetic tunnel junctions with a ferroelectric barrier

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All-oxide magnetic tunnel junctions (MTJs) incorporating functional materials as insulating barriers have the potential of becoming the founding technology for novel multifunctional devices. We investigate, by first-principles density functional theory, the bias-dependent transport properties of an all-oxide SrRuO₃/BaTiO₃/SrRuO₃ MTJ. This incorporates a BaTiO₃ barrier which can be found either in a nonferroic or in a ferroelectric state. In such an MTJ not only can the tunneling magnetoresistance reach enormous values, but also, for certain voltages, its sign can be changed by altering the barrier electric state. These findings pave the way for a new generation of electrically controlled magnetic sensors.

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I. INTRODUCTION

The control of the spin-dependent tunneling between two ferromagnetic electrodes separated by an insulating barrier has enabled enormous advances in many magnetic data storage technologies, in particular since extremely large tunneling magnetoresistance (TMR) was measured. The progress in producing magnetic tunnel junctions (MTJs) with large TMR was initially limited by the use of amorphous tunnel barriers. The situation, however, changed after the prediction and subsequent experimental realization of epitaxial MTJs. Since then, room temperature TMR in excess of 600% has been demonstrated in MgO-based devices.

In general, for amorphous barriers the spin polarization of the tunneling current and hence the TMR magnitude, depend solely on the electrodes’ density of states (DOS) at the Fermi level, \( E_F \). In contrast, perfectly crystalline tunnel barriers are wave-function symmetry selective and make the tunneling process sensitive to their electronic structure. As a result the amplitude and even sign of the TMR may depend on the barrier itself. The understanding of such a concept suggests that one can engineer the TMR by carefully selecting the insulating barriers to be epitaxially grown on magnetic electrodes. Ferromagnets and ferroelectrics are of particular interest as functional barriers.

Ferroelectric materials possess a spontaneous electric polarization whose direction can be switched by an electric field. This makes ferroelectric-based MTJs fully multifunctional devices able to respond to both electrical and magnetic stimuli. Importantly, ferroelectrics can be grown epitaxially on a variety of substrates, but in particular on other oxides. Since epitaxial growth is a prerequisite for large TMR, the prospect of all-oxide junctions appears particularly attractive. Such a type of MTJ is investigated in this article. We demonstrate theoretically a huge TMR and more importantly we show that the TMR sign can be reversed with bias, at a critical bias which depends on the ferroic state of the barrier. Our results are rationalized in terms of the band-structure match between the ferroelectric insulator and the ferromagnetic electrodes.

II. COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations are performed with the local basis set code SIESTA. Structural relaxation is obtained with the generalized gradient approximation (GGA) of the exchange and correlation functional. This gives a satisfactory device geometry, but it produces a rather shallow band alignment mainly because of the DFT-GGA gap problem. This is problematic when applying a bias across the junction as the conduction band will quickly become populated leading to an underestimation of the breakdown electric field. To make up for this shortfall the electronic structure used for the transport calculations is that obtained with the atomic self-interaction correction (ASIC) scheme, which improves drastically the electronic properties of both bulk BaTiO₃ and SrRuO₃ while increasing the electric field at which the device will breakdown. Unfortunately the approximate ASIC energy functional is not sufficient to produce good structural parameters and, in particular, the BaTiO₃ ferroelectric state cannot be stabilized. This is a current limitation of the method, which otherwise has been successful in predicting the electronic properties of oxides. For this reason we perform ASIC transport calculations at the GGA relaxed structural parameters to provide the most realistic junction description. For all the calculations we use a 6 × 6 × 1 \( k \)-point Monkhorst-Pack mesh to converge the density matrix.

Electron transport is computed with the SMEAGOL code, which combines the nonequilibrium Green’s function scheme with DFT. Since SMEAGOL interfaces SIESTA as the DFT platform, we employ here the same parameters used for the total energies calculations. In brief, the total electronic current is given by

\[
I^\sigma(V) = \frac{e}{\hbar} \int dE T^\sigma(E; V) [f_L - f_R].
\]

where \( \sigma \) labels the spin (↑, ↓), \( T^\sigma(E; V) \) is the energy-dependent transmission coefficient for the bias \( V \), \( f_L/R \) is the Fermi distribution function evaluated at \( E - \mu_L/R \), and \( \mu_L/R = E_F \pm \frac{V}{2} \) is the chemical potential of the left/right electrode. If the junction is perfectly translational invariant in the plane orthogonal to the transport direction, \( T^\sigma \) is obtained by integrating the \( \vec{k} \) dependent \( T^\sigma_{\vec{k}} \) over the two-dimensional (2D) Brillouin zone of volume \( \Omega_{BZ} \).

\[
T^\sigma(E, V) = \frac{1}{\Omega_{BZ}} \int d\vec{k} T^\sigma_{\vec{k}}(E; V). \tag{2}
\]
$T^\sigma (E, V)$ is evaluated on a $100 \times 100 \times 1 k$-point Monkhorst-Pack mesh for the zero-bias calculations and on a $24 \times 24 \times 1 k$-point mesh for the bias calculations. No sensible changes in $T^\sigma (E, V)$ were found when enlarging these $k$-point meshes.

### III. STRUCTURE

We perform an initial relaxation of bulk BaTiO$_3$ and SrRuO$_3$ under an in-plane compressive strain, emulating the common epitaxial growth on SrTiO$_3$, to find the relaxed out-of-plane lattice constant. The relaxed cells are then used to construct the transport supercell, which comprises six BaTiO$_3$ unit cells ($\sim 2.5$ nm) sandwiched at either side by three SrRuO$_3$ ones. The SrRuO$_3$/BaTiO$_3$ interface is SrO/TiO$_2$ with respect of the O atoms in the same plane, being the stack direction. The device geometry is presented in the lower part of the figure.

The atomic relaxed displacements $\delta$ with respect to the planar O positions are shown in Fig. 1. At the center of the the BaTiO$_3$ slab Ti displaces by 0.14 Å, which is significantly smaller than the value of 0.23 Å of bulk BaTiO$_3$ experiencing the same strain. Note that GGA overestimates the volume and atomic distortions associated with ferroelectricity in BaTiO$_3$ resulting in a “supertetragonal” structure. Such an overestimation, while resulting in a polarization greater than the experimental one, will not have a significant qualitative effect on our results. The interfacial SrRuO$_3$ layers, as expected, also contribute to the polarization.

### IV. RESULTS AND DISCUSSIONS

#### A. Band structure and symmetries

The symmetry of the electronic bands of both the ferromagnetic electrodes and the insulating spacer dictates the transport properties. A wave function, whether propagating or evanescent, is described in terms of irreducible representations of the crystal’s symmetry group. For a cubic space group, the $\Gamma_1$ symmetry transforms as a linear combination of $\Gamma_1$, $\Delta_1$, $\Delta_2$, $\Delta_3$, $\Delta_4$, $\Gamma_2$ and $\Gamma_3$ states. Finally, the $\Delta_5$ state is available, in contrast to previous DFT calculations, where both minority ($\downarrow$) $\Delta_5$ and majority ($\uparrow$) $\Delta_1$ bands were found. Such a discrepancy is due to the use of the GGA functional in Ref. 10, which underestimates the Ru $d$ manifold exchange splitting. Note that a large spin splitting is expected based on point contact Andreev reflection experiments.

In the right panel of Fig. 2 we plot the BaTiO$_3$ real and complex band structure. In contrast to MgO, where states with $\Delta_3$ symmetry decay significantly faster than those with $\Delta_1$ (Ref. 1), in NFE BaTiO$_3$ the $\Delta_1$ and $\Delta_5$ symmetries have comparable decay rates. In particular, close to the valence band top the slower decay rate is for $\Delta_1$, while the situation is reversed at the conduction band minimum. The enlargement of the band gap associated with the FE order results in an increased decay rate for all the symmetries. The effect is more pronounced for $\Delta_5$ close to the top of the valence band where now the $\Delta_1$ symmetry primarily contributes to the tunnel conductance.

#### B. Zero-bias transport properties

We begin our analysis of the transport properties from the NFE structure by showing $T(E)$ at zero bias for the parallel (PA) and antiparallel (AP) magnetic alignment of the electrodes (Fig. 3). In the PA configuration $T(E)$ close to $E_F$ is dominated by the minority spin channel. This is expected from the band structure of SrRuO$_3$, which presents only a
The spin-polarized current for both the PA and AP configurations and for both the NFE (top panel) and FE (middle panel) structures are shown in Fig. 4, where we focus on the low voltage region in which the current is due entirely to tunneling (the broader I-V are displayed in the insets). The most distinctive feature emerging from the I-V curves is the presence of negative differential resistances (NDR) for the PA alignment, originating from the movement of the $\Delta_1 \uparrow$ band edge with $V$. Because of the NDR the relative magnitude of the current for the parallel ($I_{PA}$) and antiparallel alignment ($I_{AP}$) can be reversed (i.e., the TMR changes sign with $V$). This is demonstrated in the lower panel of Fig. 4, where we present the “pessimistic” TMR ratio, $\text{TMR} = (I_{PA} - I_{AP})/(I_{PA} + I_{AP})$.
as a function of bias. Clearly TMR sign inversion is observed for both the NFE and the FE junctions for voltages in the range 0.7–0.9 V. Furthermore for \( V \approx 0.7 \) V the TMR for the NFE junction is positive, while that of the FE one is negative, meaning that subtle changes in the barrier electronic structure, such as those induced by ferroelectricity, are sufficient to change the sign of the TMR. Note also that the TMR values reported here are actually extremely large. For instance, for both the NFE and FE junctions and voltages \( |V| < 0.4 \) V the optimistic TMR \([(I^{\text{PA}} - I^{\text{AP}})/I^{\text{AP}}]\) is around 5000%.

The \( I-V \) curve can be rationalized by looking at the dependence of \( T(E) \) on the bias,\(^2\) which is presented in Fig. 5. This is mainly determined by the shift of the electrodes’ \( \Delta_1 \) and \( \Delta_5 \) band edges with \( V \): for positive voltage the band structure of the left electrode is shifted by \(+eV/2\) (\( e \) is the electron charge) and that of the right one by \(-eV/2\). At a given energy a large \( T \) is found only if a band of the same symmetry and spin is found in both electrodes at that energy. For PA alignment at \( V = 0 \), the minority spins dominate the transmission up to 0.3 eV, after which one encounters the \( \Delta_5 \) upper band edge and \( T \) is drastically reduced. As \( V \) is applied, the \( \Delta_5 \) band edge is shifted to lower energies in the right electrode (for \( V > 0 \)), so that for \( V = 0.6 \) V the high transmission region extends only up to \( E_F \), and for \( V = 1.2 \) V it extends only up to \( E_F - 0.3 \) eV. This is the origin of the NDR found for the PA alignment. In contrast for the AP configuration \( T \) is small for energies below 0.1 eV after which it drastically increases because of the \( \Delta_1 \) conduction bands (see Fig. 3). With increasing \( V \) the \( \Delta_1 \) band in the right electrode is shifted to lower energies, so that there is a rather large transmission inside the bias window, and eventually the AP current therefore becomes larger than the PA one. This results in the TMR sign change at about 0.7–0.9 V.

### D. Effect of ferroelectric ordering

The main effect of the ferroelectric order on the transport is an increase of the BaTiO\(_3\) band gap (i.e., an increase of the \( \Delta_1 \) and \( \Delta_5 \) decay coefficients, see Fig. 2). In particular, states with \( \Delta_5 \) symmetry decay significantly faster in the FE MTJ with respect to the NFE one. This results in a global reduction of the transmission although other general features remain rather similar in the two cases. The comparison between \( T(E; V) \) for the FE and NFE junctions is also presented in Fig. 5. Below \( E_F \) one may note a substantial reduction of the transmission when going from NFE to FE for both PA and AP alignment as a consequence of the increased \( \Delta_5 \) decay rate.

In Fig. 6 the \( k \)-resolved transmission coefficient is plotted over the full 2D Brillouin zone perpendicular to the transport direction at the Fermi level. Contributions to the majority transmission is mainly from the band edges. In contrast, transmission through the minority spin is centered around the \( \Gamma \) point, with the region between \( \Gamma \) and \( X \) also contributing, reflecting the \( d \)-state symmetry available at \( E_F \). As expected, the highest transmission is associated with the \( \Gamma \) point while transmission from the Brillouin zone edge is up to four orders of magnitude smaller across a range of energies (not shown). Ferroelectric ordering does not change the symmetry of the tunneling transmission in the \( k_x-k_y \) plane.

### V. CONCLUSION

In conclusion, we have demonstrated huge TMR in an all-oxide ferroelectric MTJ, the sign of which can be inverted as the applied bias increases. Furthermore, the sign inversion occurs at different voltages for different ferroic states of the barrier. Our finite-bias results are explained in terms of the electrodes and the barrier band structures. The possibility to control the TMR by manipulating the ferroic state of the barrier in an MTJ opens a potential avenue for the electrical control of magnetic devices.

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